PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2001-093325

(43)Date of publication of application : 06.04.2001

(51)Int.Cl.

H01B 1/08
B01D 71/02
C01G 49/00
G01N 27/404
H01B 1/06
// H01M 8/02

(21)Application number : 11-273353

(22)Date of filing : 27.09.1999

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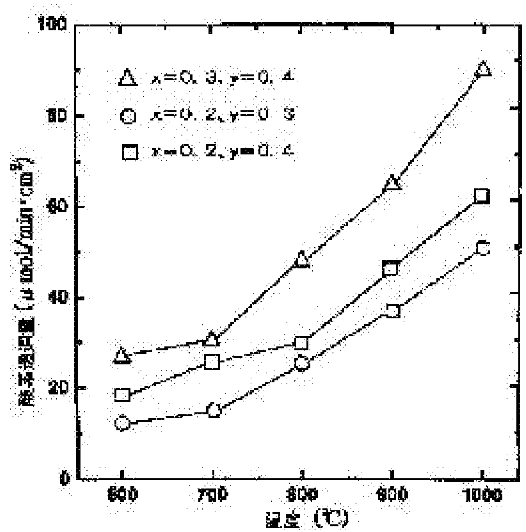
(54) $LaGaO_3$ BASED ELECTRON-OXYGEN ION MIXTURE CONDUCTOR AND OXYGEN TRANSMISSIVE FILM USING IT

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a $LaGaO_3$ electron-oxygen ion mixture conductor having oxygen ion conductivity, electron conductivity and oxygen transmissivity and to provide an oxygen transmissive film having excellent performance of transmitting oxygen with only a difference in oxygen partial pressure.



SOLUTION: La_2O_3, $SrCO_3$, Ga_2O_3, Fe_2O_3 are mixed at a preset stoichiometric ratio, the mixture is calcined at 1000°C in an atmospheric air for six hours and the obtained calcination is crushed, and then sufficiently mixed again and fired at 1500°C in an atmospheric air for six hours. The sintered body is processed with polishing to a preset size to obtain an oxygen transmissive film. The oxygen transmissive film can transmit oxygen from a higher side to a lower side of oxygen concentration and have a oxygen transmission amount of 89μmol/cm2.min.

CLAIMS

[Claim(s)]
[Claim 1]Have a Perovskite type crystal structure and it is expressed with general formula $(La_{1-x}M_x)(Ga_{1-y}Fe_y)O_{3-\mathrm{delta}}$, A $LaGaO_3$ system electronic-oxygen ion mixed conductor, wherein M is at least one sort in Sr, Ca, and Ba and y is 0.2-0.6.
[Claim 2]The $LaGaO_3$ electronic-oxygen ion mixed conductor according to claim 1 whose above-mentioned M is Sr and whose above-mentioned x is 0.05-0.6.
[Claim 3]Have a Perovskite type crystal structure and it is expressed with general formula $(La_{1-x}M_x)(Ga_{1-y}Fe_y)O_{3-\mathrm{delta}}$, M consists of a $LaGaO_3$ system electronic-oxygen ion mixed conductor which is at least one sort in Sr, Ca, and Ba, An oxygen transmission film characterized by the ability to make oxygen penetrate toward a low field from a high field of oxygen tension without forming an electrode in this $LaGaO_3$ system electronic-oxygen ion mixed conductor.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention]This invention relates to the oxygen transmission film which used a $LaGaO_3$ system electronic-oxygen ion mixed conductor (only henceforth a "$LaGaO_3$ system mixed conductor"), and it. In detail a Perovskite type crystal structure to a part of La site of the $LaGaO_3$ system sintered compact which it has Sr, Ca and Ba dissolve, and Fe is dissolving to a part of Ga site, and it is related with the $LaGaO_3$ system mixed conductor possessing the mixed-ions conductivity which consists of the outstanding oxygen ion conductivity and electron conductivity. It is related with the $LaGaO_3$ system mixed conductor which has the outstanding reduction-proof nature and has big oxygen permeability by leaps and bounds. It is related with the oxygen transmission film using this $LaGaO_3$ system mixed conductor. The $LaGaO_3$ system mixed conductor of this invention can be used as a sensor, an electrode, an oxygen transmission film, etc. The oxygen transmission film of this invention can be used as a deoxygenation film for partial oxidation of hydrocarbon.
[0002]
[Description of the Prior Art]There are an electron, a hole, and ion in the electron carrier in a solid. In this invention, that to which these can be moved simultaneously is named generically, and an electronic-oxygen ion mixed conductor is called. In addition to the application to a sensor, an electrode, etc., the application to an oxygen transmission film is expected from this electronic-oxygen ion mixed conductor. Until now, materials, such as a $LaCoO_3$ system, a $LaFeO_3$ system, or a $SeFeO_3$ system, are known as an electronic-oxygen ion mixed conductor. However, each of such materials has little oxygen transmission quantity. The electronic-oxygen ion mixed conductor itself is easy to be returned, and the use in hypoxia part

pressing down is difficult. The method of manufacturing synthesis gas by carrying out partial oxidation of the CH_4 now attracts attention from the viewpoint of upgrading of methane. It is necessary to separate oxygen from the air supplied, and material which can convey oxygen stably under the large oxygen tension of CH_4-air is desired in this method.

[0003]From the former, a $LaGaO_3$ system sintered compact is a high material of oxygen ion conductivity.

Having reduction-proof nature is known, and it can use by forming an electrode in both sides of a $LaGaO_3$ system sintered compact as a solid oxide fuel cell which has the power generation characteristic outstanding in the low temperature region as indicated by JP,9-161824,A.

An electrode is attached to the solid electrolyte which consists of this $LaGaO_3$ system sintered compact, and it becomes possible by forming an external circuit to make oxygen penetrate to a low side from the high oxygen tension side.

[0004]As indicated by Chemistry of Materials 11 (1999) 2081-2088, It is known that oxygen can be made to penetrate from the high oxygen tension side to a low side, without electron conductivity's becoming large and impressing voltage if Co is made to dissolve to Ga site of $LaGaO_3$. However, there is little transmission quantity of oxygen in 1000 ** as about 30micromol/cm^2 and min.

[0005]

[Problem(s) to be Solved by the Invention]This invention makes it a technical problem to provide the $LaGaO_3$ system mixed conductor which has the outstanding oxygen permeation performance and is provided with high reduction-proof nature. And this invention makes it a technical problem to be able to make oxygen penetrate also in low temperature comparatively, and for especially the oxygen transmission quantity to provide many oxygen transmission films by leaps and bounds, without forming an electrode.

[0006]

[Means for Solving the Problem]A $LaGaO_3$ system mixed conductor of the 1st invention, It has a Perovskite type crystal structure, and is expressed with general formula $(La_{1-x}M_x)(Ga_{1-y}Fe_y)O_{3-\mathrm{delta}}$, M is at least one sort in Sr, Ca, and Ba, and y is characterized by being 0.2-0.6.

[0007]The above "$LaGaO_3$ system mixed conductor" consists of a perovskite type crystalline lattice based on $LaGaO_3$, it is replaced by kind at least and some La in this crystalline lattice is the sintered compacts of Sr, Ca, and Ba in which a part of Ga is replaced by Fe. By making M dissolve to La site, by raising oxygen ion conductivity and making Fe dissolve to Ga site, electron conductivity can be raised and it can be considered as a mixed conductor by it in this

invention. Especially when Fe is made to dissolve compared with Co which has the same character, the amount of dissolution of M can be made to increase. However, "electron conductivity" shall be used for a meaning containing hole conduction nature in this invention.
[0008]In a $LaGaO_3$ system mixed conductor which has a Perovskite type crystal structure, although the oxidation number of La and Ga is usually +3, respectively, With a $LaGaO_3$ system mixed conductor of this invention, when the stable oxidation number makes M which is +2 dissolve to this La site, an oxygen deficiency is formed into a crystalline lattice and it is thought that oxygen ion conductivity is improving by this. If oxygen tension becomes high when Fe whose stable oxidation number is +3 is made to dissolve to Ga site, the oxidation number of this Fe will be set to +4, and a hole will be formed. It is thought that electron conductivity outstanding by this is revealed.
[0009]It is preferred that an ion radius under crystal of a $LaGaO_3$ system mixed conductor is metal near it of La as the above "M." Thereby, M dissolves easily to La site under crystal. Therefore, M can be set to Sr, Ca, and Ba. This is the same also about an ion radius under crystal of Ga and Fe.
[0010]As M, the ion radius of Sr nearest to an ion radius of La is preferred like the 2nd invention. As for x showing a quantitative ratio of Sr which dissolves to La site, it is preferred that it is 0.05-0.6, and it is more preferred that it is 0.2-0.4. Since an effect by having made M dissolve to La site that this x is less than 0.05 is not fully acquired, it is not desirable. If this x exceeds 0.6, when M not dissolving deposits in a mixed conductor as an oxide etc. and forms another phase, since oxygen ion conductivity does not fully improve, it is not desirable.
[0011]The above "y" of the 1st invention expresses a quantitative ratio of Fe which is dissolving to Ga site. This y is 0.2-0.6 and being referred to as 0.25-0.45 is preferred. Since an effect by having made Fe dissolve to Ga site that this y is less than 0.2 is not fully acquired, it is not desirable. If this y exceeds 0.6, when Fe not dissolving deposits in a mixed conductor as an oxide etc. and forms another phase, since oxygen ion conductivity does not fully improve, it is not desirable.
[0012]As for a value of these x and y, it is [x] preferred respectively that 0.05 to 0.6 and y are 0.2-0.6, and it is more preferred that x is 0.2 to 0.4, and y is 0.25-0.45. The above "delta" is a value which changes with the quantitative ratios of M and Fe which dissolve to La site and Ga site. Therefore, "3-delta" means that 3 times the amount is not contained in a crystalline lattice to $(Ga_{1-y}Fe_y)$ correctly [an oxygen atom in the above-mentioned general formula] $(La_{1-x}M_x)$ in a mol ratio.
[0013]Oxygen transmission quantity in particular of this $LaGaO_3$ system mixed conductor is not limited, but is so preferred that it is large, and can make oxygen transmission quantity (it

expresses also T_{1000} hereafter.) at the time of measuring in 1000 ** more than 30micromol/cm^2 and min. It can be made more than 50micromol/cm^2 and min, and can be especially made more than 70micromol/cm^2 and min. (A peak price is more than at least 90micromol/cm^2 and min.)

[0014]This oxygen transmission quantity a $LaGaO_3$ system mixed conductor of this invention 15.7 mm in diameter. Fabricate to 0.5-mm-thick discoid and the whole surface of this disk touches dry air of rate-of-flow 50 cc/min, When other sides touch nitrogen of rate-of-flow 50 cc/min (only henceforth a "nitrogen-air processing subsystem"), it is a value at the time of asking by measuring quantity of oxygen penetrated from this dry air side to the nitrogen side. This oxygen transmission quantity can be made more than 250micromol/cm^2 and min, when the whole surface touches methane and other sides touch air (only henceforth a "methane-air processing subsystem"), in order to be dependent on an oxygen tension difference.

[0015]When x is set to 0.25 and this $LaGaO_3$ system mixed conductor sets y to 0.4 in a nitrogen-air processing subsystem, T_{1000} can be made more than 80micromol/cm^2 and min. T_{1000} can be made more than 90micromol/cm^2 and min by setting x to 0.3 and setting y to 0.4.

[0016]A $LaGaO_3$ system mixed conductor of this invention has high reduction-proof nature. When put to reducing atmosphere, a mixed conductor is hard to be returned, and this reduction-proof nature means that a crystal structure of a $LaGaO_3$ system mixed conductor can be maintained. This reduction-proof nature can evaluate a $LaGaO_3$ system mixed conductor by a weight change by putting to a reducing atmosphere. Stability in a reducing atmosphere is so high that there are few these weight changes. Differential thermal analysis (only henceforth "TG-DTA") can estimate reduction-proof nature. For example, it can evaluate by laying a $LaGaO_3$ system mixed conductor in planchet of a differential thermal analyzer, heating and carrying out temperature up, passing nitrogen reference gas which does 10 volume % content of carbon monoxide at 200 cc/m, and measuring the weight change. In such measurement, even if a $LaGaO_3$ system mixed conductor of this invention is a case where temperature up is carried out to 30-900 **, the weight change is as low as 0.1% or less (0.09 more% or less), and has sufficient reduction-proof nature.

[0017]In a $LaGaO_3$ system mixed conductor of the 1st invention - the 2nd invention, in order to make a Perovskite type crystal structure form, in order to make each element dissolve to La site and Ga site, big thermal energy is needed further. Therefore, it is preferred to perform two

calcination or more by relatively high temperature. The end of precursor powder it specifically consists of a compound containing Sr, Ca, Ba, La, Ga, Fe, etc. is mixed in predetermined proportion, After powdering a temporary-quenching thing obtained by carrying out temporary quenching for 3 to 10 hours at temperature of 800-1200 ** in the atmosphere and fabricating this, it can obtain by calcinating at temperature of 1350-1550 ** in the atmosphere for 3 to 10 hours. Especially a thing for which each powder uses a thing excellent in dispersibility mixed uniformly as this end of precursor powder is preferred.

[0018]This uniform dispersion can be attained by a mortar etc. being sufficient and mixing powder which consists of each metallic compounds. in this case, as each metallic compounds, a compound which turns into each oxide of La, Sr, Ca, Ba, Ga, and Fe with heating of each oxide of La, Sr, Ca, Ba, Ga, and Fe, carbonate, hydroxide, a composite metal oxide, composite metal carbonate, an oxalate, etc. is used -- things can be carried out.

[0019]Uniform dispersion of each powder can be carried out more also by using a coprecipitation method and preparing the end of precursor powder. This coprecipitation is settling simultaneously a compound containing these metal from a solvent in which two or more sorts of metal ions etc. live together, and according to the coprecipitation method using this, powder mixture excellent in dispersibility containing two or more sorts of these metallic elements can be made to generate. As a solvent used in a coprecipitation method, water, an organic solvent, its mixed solvent, etc. can be used. As a compound which generates this metal ion, what dissolves each nitrate of La, Sr, Ca, Ba, Ga, and Fe, sulfate, a chloride, etc. in a solvent, and coprecipitates under predetermined conditions can be used. When using an organic solvent, an organic metallic compound can also be used. These metal ions can be settled by heating hydrolysis by addition of alkali, such as ** sodium hydroxide, or ammonia, and addition of water of ** large quantity, addition of ** organic solvent, and if needed etc.

[0020]A $LaGaO_3$ system mixed conductor of this invention has a hole in a mixed conductor, as shown in drawing 2. A diameter of this hole is 0.5-30 micrometers, and it is not preferred in order not to keep sufficient airtightness not desirable since a mechanical strength will fall, if too large [this hole is too large, or] (i.e., if the degree of precision is low), but for the gas itself to pass this mixed conductor. When x is 0.05 to 0.6 and y is 0.2-0.6, not less than 95% of theoretical density can be made to sinter in a $LaGaO_3$ system mixed conductor of this invention. As a result, density can be made more than 6 g/cm^3 (7 or more [Further 6.5 or more especially]).

[0021]An oxygen transmission film of the 3rd invention has a Perovskite type crystal structure, and is expressed with general formula $(La_{1-x}M_x)(Ga_{1-y}Fe_y)O_{3\text{ - delta}}$, M can make oxygen penetrate toward a low field from a high field of oxygen tension, without consisting of a $LaGaO_3$ system mixed conductor which is at least one sort in Sr, Ca, and Ba, and forming an

electrode in this $LaGaO_3$ system mixed conductor.

[0022]In particular thickness, shape, etc. of the above "oxygen transmission film" are not limited. Oxygen transmission quantity per unit time can be enlarged so that this thickness becomes small, but it is usually preferred that it is 10-3000 micrometers, and it is so desirable that it is thin. This oxygen transmission film can be used for a predetermined base surface, forming it, for example.

[0023]As for a penetration of oxygen in this oxygen transmission film, it is preferred that happen if an oxygen tension difference arises between this film, and this penetration occurs also in low temperature especially. A partial pressure in a high field (field where oxygen permeates) of oxygen tension between oxygen transmission films this oxygen tension, It is good in their being 10 or more times to a partial pressure in a low field (field where oxygen is emitted) of oxygen tension, it is preferred that it is more than 10^5 double, and it is more preferred that it is more than 10^{10} double. Thereby, much oxygen can be made to penetrate. Oxygen transmission quantity can also be raised by forming an electrode. As this electrode, metal, such as Ag and Pt, a $LaNiO_3$ system oxide, a $LaCoO_3$ system oxide, a $LaFeO_3$ system oxide, etc. can be mentioned.

[0024]T1000 measured in a nitrogen-air processing subsystem with the above measuring methods so preferably [although oxygen transmission quantity in particular of this oxygen transmission film is not limited] that this quantity is large, It can be made more than 30micromol/cm^2 and min, and also T1000 can be made more than 50micromol/cm^2 and min, and can be especially made more than 80micromol/cm^2 and min.

[0025]

[Embodiment of the Invention]Hereafter, an example explains this invention concretely.

Example 1 (evaluation by presentation)

** La_2O_3 of not less than 99% of the purity by which production marketing of the $LaGaO_3$ system mixed conductor is carried out, Each powder of $SrCO_3$, Ga_2O_3, and Fe_2O_3, x and y in general formula $(La_{1-x}Sr_x)(Ga_{1-y}Fe_y)O_{3-delta}$ -- the examples 1-5 of an experiment of Table 1 -- weighing was carried out so that it might become a stoichiometric ratio [like], and dry blending was carried out for 1 hour using the alumina mortar. The end of precursor powder it was obtained was put into the alumina crucible, and temporary quenching was carried out at the temperature of 1000 ** for 6 hours in the atmosphere.

[0026]

[Table 1]

表1

		焼結体組成		装置温度（℃）			
				700	800	900	1000
				酸素透過量（μmol／cm^2・min）			
実験例	1	x=0.2	y=0.4	22.596	30.095	44.900	61.718
	2	x=0.25	y=0.4	28.256	40.331	59.521	79.509
	3	x=0.3	y=0.4	30.277	47.801	64.837	89.073
	4	x=0.4	y=0.4	32.830	51.113	65.089	86.061
	5	x=0.2	y=0.3	15.150	24.660	36.420	50.340

[0027]After the alumina mortar often ground the obtained temporary-quenching powder, this powder was fabricated with the metallic mold disc-like. This Plastic solid was put into the bag made from polyurethane, and was deaerated, and the vacuum was maintained. CIP (method hydrostatic pressure press of a grade) was given for 15 minutes, pressurizing this at 2.7 t. Then, in atmospheric air, it calcinated at the temperature of 1500 ** for 6 hours, and the diameter obtained the $LaGaO_3$ system mixed conductor which is five 0.6-mm-thick kinds at about 16 mm.

[0028]** The surface of the $LaGaO_3$ system mixed conductor of the examples 1-5 of an experiment which are the oxygen permeability evaluation above and were acquired by making was ground, it fastened using the packing 3 made from heat-resistant glass among the cylinder tubes 11a and 11b made from mullite respectively, and the specimen 1a (refer to drawing 3) was produced. This specimen was further installed in the heat retaining device, and oxygen transmission quantity was measured. Dry air is supplied by a part for flow/of 50 cc from the feed port 12a (10 mm in diameter), Nitrogen is supplied by a part for flow/of 50 cc from the feed port 13a, and they are the pipes 11a and 11b (50 cm in length.). Temperature 17 cm in diameter was kept at 700 ** shown in Table 1, 800 **, 900 **, and 1000 ** for 30 minutes, and the amount of oxygen in the nitrogen discharged from the outlet 13b (10 mm in diameter) was measured by the gas chromatograph using the molecular sieve as a column. This result is written together to Table 1. The X diffraction chart of the $LaGaO_3$ mixed conductor of the examples 1-4 of an experiment to drawing 1. Mirror polishing of the surface of the $LaGaO_3$ mixed conductor of Example 3 is carried out, and correlation with x of the $LaGaO_3$ system mixed conductor which are oxygen transmission quantity and y= 0.4 in drawing 4 about correlation of oxygen transmission quantity and temperature in the taken 1000 times as many

electron microscope photographs at drawing 2 is respectively shown in drawing 5.
[0029]Since only a specific peak is observed, drawing 1 shows that the $LaGaO_3$ system mixed conductor is generated. It turns out that crystallization is good and this mixed conductor advances. This is understood also from only few 1-10-micrometer openings being accepted in drawing 2.
[0030]In x= 0.4, y= 0.4, and the device temperature of 900 **, oxygen transmission quantity is 65.1micromol/cm^2 and min, and Table 1, drawing 4, and drawing 5 show having reached 86.1micromol/cm^2 and min in 1000 **. In particular, in x= 0.3, y= 0.4, and the device temperature of 900 **, it turns out that oxygen transmission quantity is 64.8micromol/cm^2 and min, and has reached 89.1 micro mol[/cm] ^{2} and min in 1000 **, and it has the extremely outstanding oxygen permeability.
[0031]Example 2 (evaluation by thickness)
** It is made to be the same as that of the example 3 of an experiment of the production examples 1 of a $LaGaO_3$ system mixed conductor, It is x= 0.3 in general formula $(La_{1-x}Sr_x)(Ga_{1-y}Fe_y)O_{3-delta}$, and y= 0.4, Four kinds of $LaGaO_3$ system mixed conductors (about 16 mm in diameter, the thickness 0.33, 0.5 mm, 0.66 mm, and 1.0 mm) were obtained.
[0032]** Oxygen transmission quantity was measured by the same method as the oxygen permeability evaluation example 1, and correlation of the oxygen transmission quantity and thickness was **6**(ed).
[0033]Thickness is understood that there is more oxygen transmission quantity of the thinner one from drawing 6. In particular, if thickness is 0.33 mm, in the device temperature of 900 **, oxygen transmission quantity is 51micromol/cm^2 and min, and it turns out that 73 micro mol [/cm] ^{2} and min are reached in 1000 **.
[0034]Example 3 (evaluation of reduction-proof nature)
20.211 mg of $LaGaO_3$ system mixed conductors of the example 3 (x= 0.3, y= 0.4) of an experiment produced in Example 1 to the planchet which consists of platinum of a differential apparatus for thermogravimetry (the Rigaku make, form "thermostat plus") were laid. Then, a weight change and quantity-of-heat change were measured, passing the gas of the nitrogen standard which does 10 volume % content of carbon monoxide while carrying out temperature up of every 10 **/m so that a mixed conductor may be contacted at the rate of flow of 200 cc/m. This result is shown in drawing 7.
[0035]From drawing 7, weight is decreasing slightly from near 300 ** to near 680 **, and quantity of heat also serves as an endothermic at the same temperature. This expresses what oxygen ****ed by returning Fe in a mixed conductor to trivalent from tetravalence at this temperature. However, the weight change is as small as 0.1 % of the weight, and a weight

change and quantity-of-heat change are not almost in an elevated temperature further from 680 **. Therefore, it turns out that the $LaGaO_3$ system mixed conductor of this invention has high reduction-proof nature.

[0036]Example 4 (example using a coprecipitation method)

Each nitrate of La, Sr, Ga, and Fe was dissolved in pure water, the alkaline solution prepared with ammonia was dropped, and the precipitate containing each metallic element was obtained. This precipitate was dried and the end of precursor powder was obtained. This end of precursor powder was put into the alumina crucible, temporary quenching was carried out at the temperature of 600-800 ** for 6 hours in the atmosphere, and temporary-quenching powder was obtained. 1 kg of temporary-quenching powder, and these 1 l. of ethanol and 3.8 kg of balls made from silicon nitride were fed into the pot made of resin with a capacity of 4.8 l., and wet milling was carried out for 16 hours. The slurry after grinding was moved to the stainless steel ball, the water bath removed ethanol, and through and the end of precursor powder were prepared for the sieve of 60 meshes. Then, the $LaGaO_3$ system mixed conductor was obtained like Example 1.

[0037]Example 5 (use as a hydrocarbon partial oxidation machine of an oxygen transmission film)

** The $LaGaO_3$ system mixed conductor of 15.7 mm in diameter, 0.5 mm in thickness, and density 6.69 g/cm^3 (elaborated by not less than 95% of theoretical density) was obtained like the production examples 1 of a reactor. on the other hand, $La_{0.6}Sr_{0.4}CoO_3$ (it applies to 6a in drawing 8 and a field 8 mm in diameter) was looked like [the whole surface of the oxygen transmission film which consists of this $LaGaO_3$ system mixed conductor], and nickel was applied to it as a partial oxidation catalyst of hydrocarbon (it applies to 6b in drawing 8, and a field 8 mm in diameter). As shown in drawing 8, it fastened using the packing 3 made from Pyrex among the same cylinder tubes 11a and 11b made from mullite as the specimen of Example 1, and the reactor 1b was obtained.

[0038]** The reactor of hydrocarbon partial oxidation activity ****** was further installed in the heat retaining device, and hydrocarbon partial oxidation activity was evaluated. Dry air was supplied by a part for flow/of 50 cc from the feed port 12a (10 mm in diameter). And 2:1 gaseous mixture of methane and nitrogen is supplied by a part for flow/of 50 cc from the feed port 13a, The temperature of the pipes 11a and 11b (cm [in length / 50] and 17 cm in diameter) was kept at 700 **, 800 **, 900 **, and 1000 ** for 30 minutes, and the gas chromatograph analyzed the gas discharged from the outlet 13b (10 mm in diameter) at each temperature. The yield of the inversion rate of the methane obtained by that cause, carbon monoxide, hydrogen, and carbon dioxide and oxygen transmission quantity are shown in Table

2.
[0039]
[Table 2]

表２

装置温度 (℃)	CH_4転化率 (%)	CO収率 (%)	H_2収率 (%)	CO_2収率 (%)	酸素透過量 (μmol／cm^2・min)
1000	41.2	41.6	41.7	4.0	399.62
900	36.6	32.3	29.4	3.0	311.38
800	21.9	16.1	14.1	4.1	196.93
700	11.8	4.1	2.6	3.4	88.24

[0040]In this evaluation, the synthesis gas of CO/H_2=1/2 was able to be obtained with the high yield of not less than 50%, without generating carbon. There was very much especially oxygen transmission quantity in this example which is a methane-air processing subsystem, and it was T_{1000}=399.62 micro mol[/cm] ^{2} and min.
[0041]Example 6 (use as a hydrocarbon partial oxidation machine of an oxygen transmission film)
** For [CIP] 15 minutes (method hydrostatic pressure press of a grade) was given pressurizing the powder obtained by the same method as the production examples 1 of a tubular reactor with a predetermined rubber mold at 1.5 t, it calcinated at the temperature of 1500 ** in atmospheric air for 6 hours, and a tubular body the outer diameter of 14 mm, 10 mm in inside diameter, and 400 mm in length was obtained.
[0042]** The tubular type reactor 1c as shown in drawing 9 using the tubular body which is the hydrocarbon partial oxidation activity evaluation above, and was produced by making was produced. Air was made to flow between the inner tube 4 which consists of the above-mentioned tubular body, and the outer tube 5 which consists of mullites, so that it may be set to 50 cc/m. It was filled up with granular nickel system catalyst 6a in the inner tube. Heating this device in temperature of 800-1000 **, methane was made to flow from one end of an inner tube, and when the gas chromatograph analyzed the gas which flows out of the other end, the almost same result as being shown in a previous example was obtained. As a result, the $LaGaO_3$ system mixed conductor of this invention is known by that an oxygen transmission film can be used as air separation material.
[0043]In this invention, it is not restricted to what is shown in the above-mentioned concrete example, but it comes out to consider it as the example variously changed within the limits of

this invention according to the purpose and the use. That is, inevitable impurities, such as other ingredients, etc. may be contained in the range which does not have on oxygen permeability etc. substantially besides La, Sr, Ca, Ba, Ga, and Fe. The oxygen transmission film of this invention can also be made into porosity nature to such an extent that the gas itself which sufficient airtightness was maintained and introduced the surface of a hyperoxia part pressure side or both the surfaces of the oxygen transmission film does not pass. The surface area which oxygen contacts by this can be increased.

[0044]In the hydrocarbon partial-oxidation-reaction machine using the $LaGaO_3$ system mixed conductor of this invention, it can be considered as ****** (honeycomb form body) which it not only uses it by one tubular body, but collected these. In such ******, reforming efficiency can be substantially raised by [adjacent] passing hydrocarbon or air (oxygen) respectively for every pipe. Sectional shape of this tubular body can also be made into 3 which can increase a touch area not only with a round shape but the tubular body which adjoins each other more - a hexagon. The catalyst with which an inside is filled up can also use not only nickel system catalyst but a rhodium system catalyst etc.

[0045]

[Effect of the Invention]According to the 1st invention, according to making Sr, Ca, and/or Ba dissolve to La site, oxygen ion conductivity can improve and the $LaGaO_3$ system mixed conductor whose electron conductivity improved can be obtained by making Fe dissolve to Ga site. The $LaGaO_3$ system mixed conductor whose oxygen transmission quantity is very big can be obtained by improving both this conductivity. In addition, it can be considered as the high $LaGaO_3$ system mixed conductor of reduction-proof nature. According to the 3rd invention, the oxygen transmission film which can make oxygen penetrate at a predetermined temperature, without forming an electrode if there is a partial pressure difference of oxygen can be obtained by using the $LaGaO_3$ system mixed conductor of the 1st or 2nd invention.

[Translation done.]